Bond Additivity Corrections for G3B3 and G3MP2B3 Quantum Chemistry Methods

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We have developed bond additivity correction (BAC) procedures for the G3-based quantum chemistry methods, G3B3 and G3MP2B3. We denote these procedures as BAC-G3B3 and BAC-G3MP2B3. We apply the procedures to compounds containing atoms from the first three rows of the periodic table including H, B, C, N, O, F, Al, Si, P, S, and Cl atoms. The BAC procedure applies atomic, molecular, and pairwise bond corrections to theoretical heats of formation of molecules. The BAC-G3B3 and BAC-G3MP2B3 procedures require parameters for each atom type but not for each bond type. These parameters have been obtained by minimizing the error between the BAC-G3B3 and BAC-G3MP2B3 predictions and the experimental heats of formation for a 155 molecule reference set, containing open and closed shell molecules representing various functional groups, multireference configurations, isomers, and degrees of saturation. As compared to former BAC-MP4, BAC-G2, and BAC-hybrid methods, BAC-G3B3 provides better agreement with experiment for a wider range of chemical moieties, including highly oxidized species involving SO_xs, NO_xs, PO_xs, and halogens. The BAC-G3B3 and BAC-G3MP2B3 procedures are applied to an extended test suite involving 273 compounds. We assess the overall quality of BAC-G3B3 with experiments and other theoretical approaches. For the reference set, the average error for the BAC-G3B3 results is 0.44 kcal/mol as compared to 0.82 kcal/mol for the raw G3B3. For the extended test set, the average error for the BAC-G3B3 results is 0.91 kcal/mol as compared to 1.38 kcal/mol for the raw G3B3. As compared to the other BAC procedures, the improved predictive capability of BAC-G3B3 and BAC-G3MP2B3 procedures is, to a large extent, due to the improved quality of G3-based methods resulting in much smaller BAC correction terms.

I. Introduction

Efforts have been made since the 1950s to improve the accuracy of theoretical quantum chemistry methods for calculating thermochemical properties of different molecules.[1−9] Quantum chemistry methods have progressed, and corrections were added to these methods to improve the accuracy and predictive capability of estimated thermochemical properties. New hybrid methods that combine several low-level calculations have been employed to estimate the results of a high-level calculation with computational efficiency. Basis sets have evolved over time, and they have been modified to improve the accuracy of calculations. For example, size consistent complete basis set (CBS) extrapolations have been developed to correct the truncation errors due to the one-electron basis set, and quadratic CI (CBS-QCI) and coupled cluster methods [CCSD(T)] have been successfully applied to CBS approaches. A series of composite methods, referred to as Gaussian-*n* theories, have been progressively developed to optimize geometries and calculate frequencies and single point energies at increasing levels of theory and basis sets.[10−16] These predefined sets of computational methods are readily available in the Gaussian suite of programs.[17]

Gaussian-3 (G3)-based theory, the most recent in the Gaussian-*n* series, provides improved accuracy over the earlier G2 and G1 methods.[14] However, further modifications have been made in G3 theory to improve the accuracy for large nonhydrogen systems containing third row atoms such as hypervalent SF_6 and PF_5 molecules.[18] These modifications, in the form of B3LYP/6-31G(2df,p) geometry, B3LYP/6-31G(2df,p) zero point energy (ZPE), and g polarization function in the G3Large basis set for third row atoms at the Hartree−Fock (HF) level, resulted in the G3X theory.[19] The G3X theory and its variants have improved accuracy over G3 theory, however, at the cost of 10−15% additional computational time.[19] Despite their advances, there are still some nonhydrogen molecules mainly involving the third row atoms for which the heats of formation are outside the desired accuracy of 2 kcal/mol. A general and reliable systematic correction procedure is desirable to improve the predictive capability for the heats of formation of compounds involving all elements of the first three rows of the periodic table.

In the 1980s, bond additivity correction (BAC) procedures were developed for quantum chemical calculations based on the MP4 method.[20,21] Different variations of BAC-MP4 (BAC-MP4/6-311++G**, BAC-MP4 with HF geometry optimization, and BAC-MP2) were developed to reduce computational time or improve accuracy.[22,23] However, these procedures suffer from the same limitations as BAC-MP4, due to similar functional forms of the BAC corrections. Hence, BAC-G2 was developed to correct G2 methods to calculate energies for both small and large molecules.[24] This approach has also been extended to other levels of electron correlation and to a hybrid combination of MP2 and density functional theory (DFT) methods. G3-based methods have proven to be computationally faster and more accurate than G2 methods. In this paper, we address the appropriateness and value of applying the BAC procedure to the G3-based methods. We have therefore developed new BAC parameters for the G3-based methods, G3B3 and G3MP2B3.

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These methods use the B3LYP/6-31G(d) method as opposed to G3, which uses HF and MP2 methods for the geometry optimization and frequency calculations. The B3LYP method not only enhances the consistency of optimized geometries but also provides consistency with the BAC-hybrid and BAC-DFT methods.

The BAC procedure involves the atomic, molecular, and pairwise bond corrections for the heats of formation of stable molecules as well as radicals and ions. BAC parameters have been obtained by minimizing the errors between the BAC-G3B3 predictions and the experimental heats of formation for a 155 molecule reference set, containing a variety of molecules. Our reference set is larger than the one used for calculating the BAC-G2 parameters, due to the greater accuracy of the G3 methods. In addition to the reference set, we also have a test set of compounds, which is used to test the predictive capabilities of BAC parameters computed using the reference set. The test set includes many neutrals, ions, and transition state structures from the first three rows of the periodic table.

Like the BAC-G2 method, BAC-G3B3 and BAC-G3MP2B3 require parameters for each atom type but not for each bond type as in the BAC-MP4 method. The BAC-MP4 method provided excellent thermochemistry for combustion and CVD systems but could not treat ions. Furthermore, it was inadequate for systems with highly oxidized species involving SO_xs, NO_xs, and PO_xs. The BAC-G2 method attempted to correct the discrepancies for halogens but required large correction terms, which led to accumulated errors, particularly for the heats of atomization. The BAC-G3B3 and BAC-G3MP2B3 methods should provide a better base for these systems, since the G3 methods have smaller inherent and systematic errors. As we shall show, the BAC-G3B3 method provides the best estimates of thermochemistry for compounds involving the first three rows of the periodic table. Reasonably accurate experimental data are known for the thermochemistry for most of these compounds. Many of the compounds had been used earlier in the reference set to evaluate the BAC parameters for the BAC-G2, BAC-MP4, BAC-MP2, and BAC-hybrid methods.

In this work, we compile an updated reference set of heats of formation for comparing thermochemical parameters and determining BAC parameters. The result of this work is sets of parameters defining the BAC-G3B3 and BAC-G3MP2B3 procedures along with comparisons with experimental and other theoretical approaches indicating the accuracy of BAC-G3B3 and BAC-G3MP2B3 methods. The parameters developed have predictive capabilities that can be used for a variety of molecules.

This paper presents the development, application, and assessment of BAC procedures for the G3B3 and G3MP2B3 methods. The paper is organized in the following order. In section II, we describe the BAC procedures and define the different forms of corrections to heats of formation of molecules. We present the approach to estimate thermochemical properties and discuss the reference set of molecules. In section III, we present the calculated BAC-G3B3 and BAC-G3MP2B3 parameters for atom, molecular, and bond corrections. We compare the heats of formation predicted by BAC methods against experimental values and heats of formation predicted by uncorrected G3B3 and G3MP2B3 methods. We assess the overall as well as specific accuracy of BAC-G3B3 and BAC-G3MP2B3 methods in predicting the heats of formation of different compounds. We present a statistical analysis to compare the overall accuracy of various BAC procedures. For specific classes of compounds, we compare the heats of formation predicted by the BAC-G3B3 and BAC-G3MP2B3 methods against the values predicted by modified G3 methods: G3X, G3SX, and G3X2 methods. These classes of compounds mainly involve third row atoms, hypervalent species, and set A[19] compounds, triatomic and larger nonhydrogen species used in the G3/99 reference set[18] and phosphorus oxides used to assess G3X2 theory.[25,26] Finally, we analyze the predictive capabilities of BAC-G3B3 and BAC-G3MP2B3 methods for ions and transition state structures.

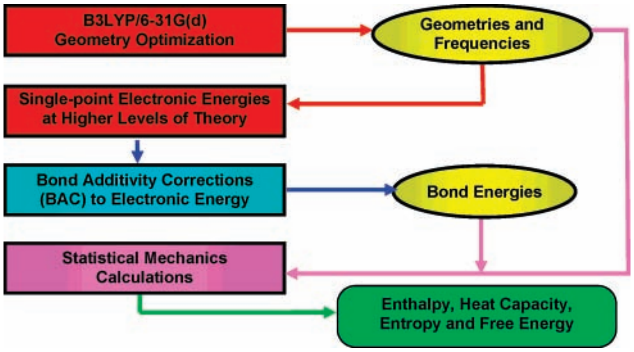

Figure 1. BAC procedure for estimating thermochemical properties.

II. BAC Procedure for Estimating Thermochemical Properties

In this section, we describe the BAC procedure for estimating the thermochemical properties: heat of formation, heat capacity, entropy, and free energy of a molecule. The overall BAC procedure and the sequence of calculations are schematically shown in Figure 1.

First, the molecular geometry is optimized and vibrational frequencies are calculated at the B3LYP level of theory using the 6-31G(d) basis set. Next, single point calculations are performed at increasing levels of theory and basis sets to obtain the raw electronic energy. BAC corrections are added to the raw electronic energy to determine the corrected electronic energy. The corrected energy is then used to derive the enthalpy, entropy, heat capacity, and free energy of the molecule. In the following subsections, we describe the details of the BAC-G3B3 and BAC-G3MP2B3 procedure.

A. G3B3 and G3MP2B3 Electronic Structure Calculations. Electronic structure calculations are performed to obtain the geometry, vibrational frequencies, and electronic energy of a molecule. Within the G3 suite of methods, we have chosen the G3B3 and G3MP2B3 methods for applying the BAC procedure. The G3B3 and G3MP2B3 methods use the B3LYP level of theory with the 6-31G(d) basis set to determine the equilibrium geometry and vibrational frequencies. We chose the B3LYP method for greater consistency (only a single geometry optimization is needed) and accuracy. In addition, the B3LYP employs the same geometry and frequency calculations used by the BAC-hybrid and BAC-DFT procedures, i.e., B3LYP/6-31G(d). The resulting vibrational frequencies are used subsequently to determine the ZPE of the molecule derived from statistical mechanics (see Figure 1).

Having determined the structure and vibrational frequencies of the molecule, single point electronic energy calculations are performed using a higher level of electronic structure theory that incorporates electron correlation. For the BAC-G3B3 method, we apply the G3B3 method, involving QCISD(T, E4T) with the 6-31G(d) basis set, MP4 with the 6-31G(2df,p) basis set, and MP2 with the GTLarge basis set. For the BAC-G3MP2B3 method, we apply the G3MP2B3 method, involving

QCISD(T) with the 6-31G(d) basis set and MP2 with the GTMP2Large basis set. The combination of geometry optimization, frequency calculation, and electronic energy calculation is performed as a single procedural step within the Gaussian suite of programs using the keywords G3B3 or G3MP2B3.

B. BAC Corrections to Electronic Energy. To correct for errors in electronic energy of the molecule, we had developed a set of empirical expressions collectively referred to as BACs:[24]

$$E_{\mathrm{BAC-correction}}(\mathrm{total}) = E_{\mathrm{BAC-atom}} + E_{\mathrm{BAC-molecule}} + \sum_{ij} E_{\mathrm{BAC-bond}}(A_iA_j) \quad (1)$$

where *ij* is summed over all of the chemical bonds in the molecule. The total correction consists of three terms: (i) an atomic correction due to all of the atoms that make up the molecule, (ii) a molecular correction due to the molecule as a whole, and (iii) bond corrections due to all of the bonds in the molecule. The correction terms are functions of the BAC parameters, which are obtained by comparing the BAC predicted heats of formation with a reference set of experimental values.

There are four kinds of BAC parameters: (i) A_{atom} (atom correction), (ii) B_{atom}, (iii) A_{ii} (bond corrections), and (iv) $K_{\mathrm{elec-pair}}$ (electron pair correction). The atom and bond correction parameters depend on the types of atom, while the electron pair correction parameter depends on the molecular spin state. The physical meanings of these parameters and their respective contributions to the atomic, molecular, and bond correction terms in eq 1 are briefly described in the following subsections.

B.1. Atomic Corrections. The atomic correction is summed over all of the atoms making up the molecule:

$$E_{\mathrm{BAC-atom}} = \sum_k A_k \quad (2)$$

The atomic correction corrects errors in the intraatomic electron correlation, which is due to the differences between atomic electronic configurations, charge and spin–orbit coupling, and core valence interactions and other relativistic effects. Atom parameters improve the accuracy of molecular predictions by shifting some of the systematic errors into the calculation of constituent elements.

B.2. Molecular Corrections. Molecular correction (second term in eq 1) corrects the error from the overall electronic structure of molecule:

$$E_{\mathrm{BAC-molecule}} = E_{\mathrm{BAC-elec-pair}} + E_{\mathrm{BAC-S2}} \quad (3)$$

$E_{\mathrm{BAC-elec-pair}}$ is the energy difference due to the spin of the molecule and the individual atoms comprising the molecule:

$$E_{\mathrm{BAC-elec-pair}} = K_{\mathrm{elec-pair}}(S_{\mathrm{molecule}} - \sum_k S_k) \quad (4)$$

S_{molecule} and S_k are spin quantum numbers for the molecule and the *k*th atom (S values for singlet, doublet, triplet, and quartet are 0, 0.5, 1, and 1.5, respectively).

Errors due to the interaction of electrons in atoms and molecules are systematic and depend on the way in which electron correlation is accounted for while computing the electronic energies of molecules. The size of the correlation error depends on the spin state of the molecule, and the errors are much larger when electrons are paired than when they are unpaired. Hence, the correction term involving $K_{\mathrm{elec-pair}}$ describes the general case of electron pairing. It needs to be noted that the molecular correction term destroys the size consistency of quantum chemistry methods. For example, the sum of the calculated energies for hydrogen and oxygen atoms is not the same as the energy of the hydroxyl radical when the two atoms are fixed at infinity.

The second term in eq 3, corresponding to $E_{\mathrm{BAC-S2}}$, depends on the spin contamination, if present, in the electronic wave function. For example, a doublet state may have a quartet state spin contamination. The spin contamination term corrects the errors arising from the open shell methods based on unrestricted HF. Because DFT methods tend not to have any significant instability, we do not include the unrestricted wave function spin correction.

B.3. Bondwise Corrections. Bondwise corrections address the systematic error from electron pairing not covered by the molecular correction term. Considering atom connectivity C–A–B–D in the molecule, correction for each bond A–B with neighbors C and D is

$$E_{\mathrm{BAC-bond}}(AB) = A_{\mathrm{AB}} e^{(-\alpha R_{\mathrm{AB}})} + \sum_C B_{\mathrm{CA}} + \sum_D B_{\mathrm{DB}} \quad (5)$$

The first correction term is a function of bond correction parameter (A_{AB}), exponent (α), and bond distance (R_{AB}). Because of the negative exponential dependence, the correction is more significant for molecules with shorter bond distances, which are common for unsaturated, dative, and hypervalent bonds. This term is important for bonds between atoms in the second and third rows. Typical examples are PF_5 and SF_6, where the heavier *p*-block elements are attached to highly electronegative elements such as the halogens or oxygen. Hence, the bond correction parameter A_{AB} plays an important role in correcting the errors in hypervalent compounds.

For the BAC-G3B3 and BAC-G3MP2B3 procedures, A_{AB} is set as the geometric mean of the A_{ii} values for the atoms A and B:

$$A_{\mathrm{AB}} = (A_{ii,\mathrm{A}} \times A_{ii,\mathrm{B}})^{1/2} \quad (6)$$

A_{ii} is dependent on the atom type and not the bond type, and the bond dependence of the correction parameter A_{AB} comes from the geometric mean of the two A_{ii} values.

The second and third terms (B_{CA} and B_{DB}) in eq 5 correct for the errors due to nearest neighbors. The correction for the nearest neighbors is the sum of the corrections for the individual neighboring atoms:

$$B_{\mathrm{CA}} = B_{\mathrm{C}} + B_{\mathrm{A}} \quad (7)$$

Because of B_{CA} and B_{DB}, the total bondwise correction is not zero when the bond distance is infinity.

C. Thermochemical Properties. Having obtained the electronic energy of the molecule, we first calculate the electronic heat of atomization:

$$E_{\mathrm{atomization}} = \sum_i^n E_i(\mathrm{atoms}) - [E_{\mathrm{ab-initio}}(\mathrm{molecule}) + E_{\mathrm{ZPE}}] \quad (8)$$

The heat of atomization is subtracted from the sum of experimental heats of formation of the atoms to yield the uncorrected heat of formation at 0 K:

$$\Delta H_{f0,\mathrm{uncorrected}} = \sum_{\mathrm{atoms}} \Delta H_{f0,\mathrm{atoms}} - E_{\mathrm{atomization}} \quad (9)$$

The total BAC correction is subtracted from the uncorrected heat of formation to yield the corrected heat of formation at 0 K:

$$\Delta H_{f0,\mathrm{BAC}} = \Delta H_{f0,\mathrm{uncorrected}} - E_{\mathrm{BAC-correction}} \tag{10}$$

Statistical mechanics is used to calculate the enthalpy, entropy, and free energy of the molecule at desired temperature. The thermochemical properties as a function of temperature can be fit to form the NASA polynomial coefficients compatible with the Chemkin thermodynamic database.[27]

Uncertainties resulting from the applicability of the BAC-G3B3 method to a given molecule are estimated using an ad hoc expression, similar to ones used in previous BAC methods.[21,24] Raw-G3B3 energies in addition to the BAC-G3MP2B3 energies are used as references to calculate the error estimate (error in kcal/mol):

$$\mathrm{error}_{\mathrm{BAC-G3B3}} = [1 + (\Delta H_{\mathrm{BAC-G3B3}} - \Delta H_{\mathrm{BAC-G3MP2B3}})^2 + (\Delta H_{\mathrm{BAC-G3B3}} - \Delta H_{\mathrm{raw-G3B3}})^2]^{1/2} \tag{11}$$

Because the raw G3B3 energies are reasonably accurate in predicting the heats of formation for most molecules, they are used as references when computing the error estimate. This helps one to identify molecules with consistently large errors due either to the raw method or to large corrections within the BAC procedure. For large error estimates, further electronic energy calculations should be applied to the given molecule at higher levels of theory and basis sets; basis set extrapolations for small basis sets are not sufficient to identify the cause of the uncertainty.

D. Reference and Test Set of Molecules. The parameters for the BAC procedure are determined by fitting the calculated heats of formation to a reference set of experimental values. The reference set of molecules consists of open and closed shell compounds representing various chemical moieties, multireference configurations, isomers, and degrees of saturation. For the BAC-G3B3 and BAC-G3MP2B3 procedures, the reference set is an extension of the one used for calculating the BAC-G2 parameters. We created an extended test set to ascertain the predictive capability of the BAC methods. The test set extends the reference set to include ions as well as additional molecules involving third row atoms, including set A[19] compounds and the nonhydrogen species (triatomic and larger) used in the G3/99 test set[18,19] as well as PO_x compounds used to assess the G3X2 theory.[25,26] Unlike the G2 method, the G3 methods provide more reliable and systematic treatment of the heats of formation for these additional third row containing molecules. The test set includes molecules for which the accuracy of experimental values may not be as well validated and thus were not included in the reference set. Including such molecules in the reference set could have an adverse effect on defining the BAC parameters. In addition, the test set includes positive and negative ions for which the predictive capability of the BAC procedure has not yet been demonstrated.

Table S1 in the Supporting Information lists the heats of formation for the reference set used in the current work, along with comparison of the values used in the previous work. Table S2 lists the heats of formation of compounds used in the extended test set. Experimental sources for the heats of formation are also cited in Tables S1 and S2. In Table 3, section III B, we also list, for convenience, the experimental heats of formation (column 2). Heats of formation of molecules in the reference set have been quite well-established experimentally.

TABLE 1: BAC-G3B3 Parameters (kcal/mol)

	$K_{\mathrm{elecpair}} = 0.318$				$K_{\mathrm{elecpair}} = 0.318$		
atom	A_{atom}	B_{atom}	A_{ii}	atom	A_{atom}	B_{atom}	A_{ii}
H	0.021	0.060	1.1500	Al	−0.70	−0.05	2.0000
B	0.050	0.010	1.1242	Si	0.003	0.058	22.3296
C	0.141	0.005	0.0000	P	−0.337	0.049	609.9930
N	0.278	0.054	0.0000	S	−0.664	0.063	503.9800
O	0.000	−0.024	45.8645	Cl	0.146	0.046	1074.3082
F	0.023	0.031	50.9352				

TABLE 2: BAC-G3MP2B3 Parameters (kcal/mol)

	$K_{\mathrm{elec\ pair}} = 0.286$				$K_{\mathrm{elec\ pair}} = 0.286$		
atom	A_{atom}	B_{atom}	A_{ii}	atom	A_{atom}	B_{atom}	A_{ii}
H	0.000	0.113	0.3259	Al	−0.575	−0.050	1.0000
B	0.030	0.004	1.3241	Si	−1.277	0.119	10.9056
C	−0.230	0.002	0.0000	P	−0.675	0.031	467.4820
N	0.092	0.081	2.2571	S	−1.622	0.064	519.0579
O	0.000	0.031	68.4380	Cl	−0.496	0.133	1172.3986
F	−0.080	0.110	59.0911				

Most of the experimental values for the reference set of molecules are the ones recently recommended by the IUPAC subcommittee.[28] The recommended values have been taken from evaluations or reviews. For compounds involving Si, P, S, Al, and B atoms, experimental values are taken from other data sources. For some compounds, the updated values recommended by IUPAC subcommittee are significantly different from the ones used in fitting the BAC-G2 parameters,[24] in particular, NH_2, HNO, CN, CH_2OH, CH_3CN, $CH_2CH{=}CH_2$, and CS. The difference in the experimental heats of formation is listed in Table S3 in the Supporting Information.

III. Results and Discussion

In this section, we present the results and assess the performance of the BAC-G3B3 and BAC-G3MP2B3 methods for the thermochemical properties for various types of molecules. The assessment is made by comparing the predicted heats of formation against experimental data as well as values predicted by many theoretical methods for different classes of compounds both in the reference set and in the extended test set of molecules.

A. BAC-G3B3 and BAC-G3MP2B3 Parameters. BAC parameters are obtained by minimizing the difference between BAC predicted heats of formation and established experimental values for the 155 molecule reference set. The resulting parameters for the BAC-G3B3 and BAC-G3MP2B3 are listed in Tables 1 and 2, respectively.

The BAC-G3B3 atom correction parameters are less than 1 kcal/mol for all of the elements, unlike the BAC-G2 atom parameters, some of which were greater than a kcal/mol (see Table 1 in ref 24). Specifically, BAC-G2 atom correction parameters for H, C, N, O, and F were 0.485, 1.081, 1.498, −0.501, and −1.942 kcal/mol, while the corresponding BAC-G3B3 parameters are 0.021, 0.141, 0.278, 0.000, and 0.023. This indicates the overall accuracy of the G3B3 methods as compared to the G2 method, especially for compounds involving interactions between second and third row elements. Because G3MP2B3 is less accurate than G3B3, particularly for third row elements, the atom correction parameters are considerably larger for the BAC-G3MP2B3 procedure.

$K_{\mathrm{elec-pair}}$ values for BAC-G3B3 (0.318) and BAC-G3MP2B3 (0.286) are smaller than that for BAC-G2 (0.860). In BAC-G2, the $E_{\mathrm{BAC-elec-pair}}$ correction terms were larger for molecules having many atoms, since the accumulation of spin quantum number for each atom resulted in a large net $E_{\mathrm{BAC-elec-pair}}$ (see

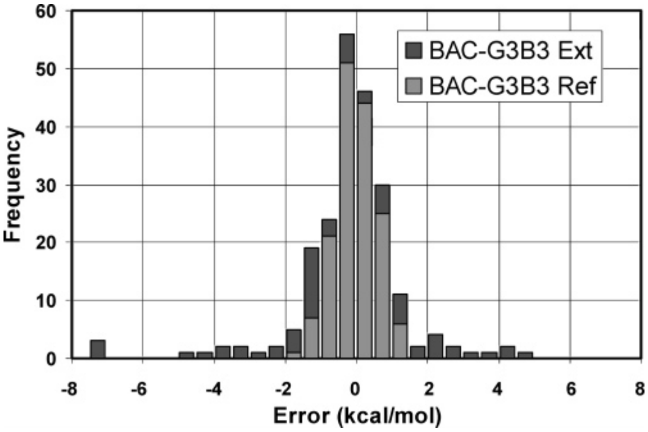

Figure 2. Frequency distribution of errors in the BAC-G3B3 heats of formation of neutrals in the test set in Table 3. The 216 neutral molecules include the 155 molecules in the reference set (BAC-G3B3 Ref) and 61 additional molecules (BAC-G3B3 Ext). Heats of formation are at 298 K.

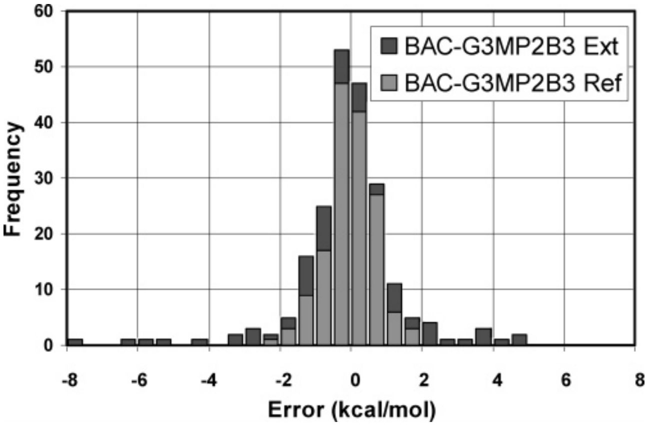

Figure 3. Frequency distribution of errors in the BAC-G3MP2B3 heats of formation of neutrals in the test set in Table 3. The 216 neutral molecules include the 155 molecules in the reference set (BAC-G3MP2B3 Ref) and 61 additional molecules (BAC-G3MP2B3 Ext). Heats of formation are at 298 K. The scale for the *x*-axis is between −8 and 8 kcal/mol for comparing Figures 2 and 3. The error for PO molecule is −11.3 kcal/mol; hence, the molecule is not included in this figure.

eq 4). However, these large corrections tended to be compensated by the large atomic corrections, $E_{\mathrm{BAC-atom}}$ (eq 2). The $K_{\mathrm{elec-pair}}$ and atom parameters are both small for BAC-G3B3 and BAC-G3MP2B3 methods. To some extent, errors due to electron pairs were accounted within raw G3 methods by means of the semiempirical HLC parameters, which were fit using the experimental heats of formation.[19] The HLC parameters were helpful in correcting the errors separately due to unpaired and paired electrons in atoms and molecules. The $K_{\mathrm{elec-pair}}$ computed in this work corrects the additional errors not covered by the HLC parameters.

B. Assessment of the BAC-G3B3 and BAC-G3MP2B3 Procedures for Reference Set of Molecules. Table 3 compares the accuracies in raw as well as BAC-G3B3, BAC-G3MP2B3, and BAC-G2 methods, by listing the deviations between theoretical and experimental heats of formation (see Tables S1 and S2 in Supporting Information for references to experimental data).

A frequency distribution histogram of the errors (theory minus experiment) for the BAC-G3B3 and BAC-G3MP2B3 methods is shown in Figures 2 and 3. The 216 neutral molecules listed in Table 3 are used in the test set, 155 molecules are used in the reference set (denoted BAC-G3B3 Ref), while the 61 additional molecules of Table 3 represent the extended set (denoted BAC-G3B3 Ext).

We performed a statistical analysis on the energy differences between theory and experiment for both the raw G3 and G2 energies and the BAC corrected energies. The average, RMS, and maximum errors in the heats of formation calculated for these methods are listed in Table 4. In the table, all errors are positive, since unsigned quantities are considered.

We first discuss the results for the reference set, for which the accuracy of the experimental values is believed to be high. The results of the extended test set are discussed separately below. From the results of the reference set in Tables 3 and 4, we observe the following.

(i) Errors in the raw G3B3 and G3MP2B3 energies are less than the corresponding errors for the raw G2 method for most of the molecules. This indicates improved inherent accuracy of the G3-based methods.

(ii) The raw G3B3 energies are more accurate than the raw G3MP2B3 energies for most of the molecules. This is consistent with the higher level quantum chemistry approaches used in G3B3 as opposed to G3MP2B3.

(iii) The BAC-G3B3 and BAC-G3MP2B3 energies are more accurate than the BAC-G2 energies for most of the molecules. The BAC-G3B3 energies are more accurate than the BAC-G3MP2B3 energies. The average, RMS, and maximum errors in the heats of formation are the least for BAC-G3B3 method. Errors in BAC-G3B3 are significantly lower than those in BAC-G2, while they are slightly lower than BAC-G3MP2B3.

(iv) The BAC procedure significantly improves the accuracy of both the G3B3 and the G3MP2B3 methods and provides consistently excellent agreements with experiments. BAC-G3B3 has reduced the average error from 0.82 to 0.44 kcal/mol and the RMS error from 1.37 to 0.56 kcal/mol.

(v) The BAC-G3MP2B3 energies are approaching the accuracies of the BAC-G3B3 energies (average error of 0.50 vs 0.44 kcal/mol), making the G3MP2B3 method a very viable method for determining the heats of formation of molecular species, particularly for larger molecules for which the G3B3 method becomes computationally expensive.

(vi) While the average error for raw G3B3 is within a kcal/mol, the maximum error (8.73 kcal/mol) is high. BAC corrections have reduced the maximum errors considerably. There is a similar improvement in the maximum error for G3MP2B3 methods.

On the basis of the reference set, the BAC-G3B3 method gives the best results. The BAC-G3B3 method is clearly preferable to BAC-G2 due to its greater accuracy. In addition, it is computationally faster. BAC-G3B3 can be applied to predict the heats of formation of large molecules with many atoms, which BAC-G2 could not handle. It should be noted that the BAC-G3MP2B3 also does remarkably well. BAC-G3MP2B3 is well-suited to be applied to even larger molecules.

As was the case for the BAC-G2 procedure, BAC-G3B3 and BAC-G3MP2B3 parameters depend only on the atoms and not the pairs of atoms present in a molecule. Only a few reference compounds containing a given element are required to determine the BAC parameters for all of the compounds containing the element. This requires a reference set that is sufficiently large to define the parameters but does not introduce artifacts in the parameters due to errors in the experimental heats of formation. In the following subsection, we discuss the larger test set and results for specific chemical groups that represent special concerns.

TABLE 3: Comparison of Raw and BAC Heats of Formation against Experimental Values at 298 K for a Reference Set of Molecules[a]

	heat of formation (kcal/mol)						
		error = theory − experiment					
neutrals	experimental	raw-G3B3	raw-G3MP2B3	raw-G2	BAC-G3B3	BAC-G3MP2B3	BAC-G2
	Reference Set						
C	171.3	−0.1	−0.1	−0.1	−0.2	0.2	−1.2
CCl_4	−22.9	−0.2	−1.9	−2.9	−0.6	−0.5	0.1
CF_4	−223.2	0.0	0.1	−5.4	0.3	0.1	0.4
CH_2 $^1A_1$	102.5	−0.8	−1.1	−1.2	−0.4	−0.4	−1.7
CH_2 $^3B_1$	93.4	−1.2	−1.4	1.2	−1.2	−1.1	−0.2
CH_2Cl_2	−22.8	1.0	0.0	−0.7	0.8	0.6	1.1
CH_2F_2	−108.3	0.1	0.1	−2.6	0.2	0.0	0.8
H_2CNH	21.6	−0.6	−0.8	−1.0	−0.3	−0.4	−1.2
CH_2NH_2	35.7	0.5	0.8	1.1	0.3	0.5	0.7
CH_2O	−26.0	−1.0	−1.0	−2.1	−0.5	−0.5	−0.8
CH_2OH	−4.3	0.1	0.3	0.4	0.2	0.4	−1.6
$CH_2(OH)_2$	−93.5	−1.0	−0.4	−2.4	−0.7	−0.5	−1.0
CH_3	35.0	−0.8	−0.7	0.0	−0.8	−0.6	−0.1
CH_3Cl	−19.6	0.4	0.0	−1.0	0.3	0.1	0.3
CH_3F	−55.6	−1.1	−1.0	−2.9	−1.1	−1.2	−0.8
CH_3NH	42.4	0.1	0.3	0.5	0.0	0.0	0.2
CH_3NH_2	−5.5	0.7	1.1	−0.1	0.4	0.3	0.3
CH_3NHNH_2	22.6	0.5	1.1	−0.6	−0.1	−0.3	−0.2
CH_3NO_2	−17.9	−1.0	0.4	−2.9	−0.7	−0.3	−0.9
CH_3O	4.2	0.1	0.3	0.5	0.3	0.3	1.8
CH_3ONO	−15.6	−1.2	−0.4	−3.1	−0.4	−0.6	−0.9
CH_3ONO_2	−28.6	−2.2	−0.2	−4.3	−1.2	−0.8	−1.0
CH_3OO $^2A''$	2.5	0.3	0.8	−0.4	0.0	−0.4	0.0
CH_3OOH	−31.3	0.5	1.2	−0.7	0.5	0.3	0.4
CH_3SH	−5.5	0.5	−0.5	0.0	0.8	0.8	0.4
CH_3SiH_3	−6.9	0.2	0.2	−0.7	−0.7	−0.7	0.6
CH_4	−17.9	−0.1	0.2	−0.8	−0.2	−0.1	−0.1
$CHCl_3$	−24.7	1.1	−0.4	−1.1	0.8	0.6	1.3
CHF_3	−166.9	0.1	0.1	−3.8	0.3	0.1	0.7
CO	−26.4	−0.6	−1.4	−1.9	−0.1	−0.6	−0.7
CO_2	−94.1	−1.6	−1.4	−2.7	−0.8	−0.4	−0.3
CS	66.6	−0.7	−3.0	−0.7	0.4	−0.6	1.4
CS_2	28.0	−3.0	−5.3	−2.2	−1.0	−1.1	−1.1
HCN	32.3	−1.7	−1.8	−1.2	−1.3	−1.0	−1.6
HCO	10.3	−0.9	−1.3	−1.1	−0.5	−0.7	−0.1
HCOOH	−90.5	−0.6	−0.2	−2.1	0.1	0.4	−0.2
HNCS	30.0	−0.2	−0.9	0.5	1.0	1.5	0.6
OCS	−34.0	−2.1	−2.8	−1.8	−0.6	−0.3	−0.2
CH $^4\Sigma^-$	157.4	0.1	−0.7	3.9	−0.1	−0.5	2.3
CH_3PH_2	−4.4	0.9	0.3	0.0	0.5	0.5	0.1
CCl_2F_2	−117.9	−0.4	−1.0	−5.0	−0.5	−0.2	−0.5
C ^5S	267.7	0.1	0.2	0.4	−0.3	0.2	−1.5
CH_3OH	−48.2	−0.2	0.2	−1.3	−0.1	0.0	−0.3
$-CH_2CH_2O-$	−12.6	−0.4	−0.1	−1.4	0.1	0.1	−0.6
$-CH_2CH_2S-$	19.7	−0.9	−1.9	−1.0	−0.4	−0.3	−0.8
C_2H $^2\Sigma^+$	135.0	−0.4	−1.1	3.6	−0.2	−0.2	2.7
HCCH	54.5	−0.3	−0.8	1.2	0.2	0.3	0.6
HC(O)CHO	−50.7	−1.7	−1.5	−3.0	−0.7	−0.3	−1.0
H_2CCH_2	12.5	−0.3	−0.9	0.1	0.0	−0.2	−0.2
C_2H_5	28.9	−0.4	−0.3	0.8	−0.4	−0.2	0.3
CH_2CO	−11.4	−1.1	−1.2	−0.8	−0.4	−0.1	0.0
$CH_3CH_2NH_2$	−11.4	−0.2	0.2	−0.9	−0.5	−0.5	−0.9
CH_3CH_2OH	−56.1	−0.4	0.0	−1.3	−0.3	−0.2	−0.6
CH_3CH_2ONO	−24.8	0.2	1.0	−1.6	1.1	0.9	0.3
CH_3CH_2SH	−11.0	0.4	−0.6	0.1	0.7	0.8	0.1
CH_3CHO	−39.6	−0.6	−0.4	−1.5	0.0	0.2	−0.3
CH_3CO	−2.4	−0.5	−0.6	−0.7	−0.1	0.0	0.1
CH_3NHCH_3	−4.4	0.5	1.0	−0.5	0.1	0.1	0.0
CH_3OCH_3	−44.0	−0.7	−0.1	−2.2	−0.3	−0.3	−0.2
CH_3OOCH_3	−30.0	0.3	1.3	−1.6	0.7	0.5	0.4
CH_3SCH_3	−8.9	0.3	−0.6	−0.4	0.7	0.6	0.9
$OS(CH_3)_2$	−36.1	1.8	1.3	1.2	0.7	0.5	0.1
$SiH_2(CH_3)_2$	−22.7	1.4	1.5	0.9	0.4	0.3	2.2
CH_3COOH	−103.3	−0.5	0.1	−1.9	0.0	0.6	−0.2
CH_3CH_3	−20.1	−0.2	0.1	−0.7	−0.2	−0.2	−0.3
$-CH_2CH_2CH_2-$	12.7	0.5	0.4	0.7	0.5	0.7	−0.5

TABLE 3 (Continued)

	heat of formation (kcal/mol)						
		error = theory − experiment					
neutrals	experimental	raw-G3B3	raw-G3MP2B3	raw-G2	BAC-G3B3	BAC-G3MP2B3	BAC-G2
				Reference Set			
$-CH_2OCH_2OCH_2O-$	−113.2	−0.9	0.5	−3.1	0.2	−0.4	−0.6
CH_2CCH_2	45.6	−0.8	−1.8	0.7	−0.4	−0.7	−0.1
CH_2CHCH_2	40.8	−0.9	−1.0	0.9	−0.6	−0.1	1.4
CH_3CCH	44.4	−0.5	−1.0	1.1	−0.1	0.0	0.6
$CH_3CH_2CH_3$	−25.0	−0.3	−0.1	−0.7	−0.3	−0.2	−0.8
CH_3CH_2CHO	−44.8	0.3	0.5	−0.6	0.8	1.1	0.2
CH_3CHCH_2	4.8	−0.3	−0.8	0.3	0.0	−0.2	−0.3
CH_3COCH_3	−51.9	−0.3	0.0	−1.3	0.1	0.5	−0.3
$CH_3CH_2CH_2CH_3$	−30.1	−0.2	−0.1	−0.6	−0.3	−0.2	−0.8
$CH_2CHCHCH_2$	26.1	0.1	−1.1	1.7	0.8	0.4	0.4
CH_3CCCH_3	34.7	0.2	−0.2	1.7	0.4	0.6	1.2
$CH_3CH(CH_3)_2$	−32.4	0.1	0.2	−0.4	0.1	0.2	−0.8
C_6H_{12}	−29.5	0.0	−0.2	0.5	−0.7	−0.7	−1.8
C_6H_6	19.8	0.3	−1.7	3.6	1.1	0.8	0.6
OH	8.9	−0.6	−0.8	0.1	−0.6	−0.8	−0.2
H	52.1	0.0	0.0	0.0	−0.1	0.0	−0.5
HCl	−22.1	0.4	−0.3	−0.4	−0.2	0.1	−0.3
HF	−65.3	0.0	−0.2	−0.9	−0.2	−0.1	0.0
HN_3	70.3	−0.3	0.1	−0.5	−0.1	0.4	−1.2
HNO	27.0	−1.6	−1.7	−2.5	−1.1	−1.6	1.5
HO_2 $^2A''$	3.5	−0.5	−0.3	−0.2	−1.1	−1.5	−0.6
$HONO_2$	−32.3	−0.5	1.1	−2.2	0.1	0.4	0.2
HONO cis	−18.3	−0.2	0.2	−1.6	0.4	0.1	−0.3
HONO trans	−18.8	−0.3	0.1	−1.7	0.2	−0.1	−0.3
NH $^3\Sigma^-$	84.1	−0.1	−0.5	2.1	0.0	−0.4	0.9
HOCl	−18.7	1.5	1.4	0.3	0.2	0.3	−0.2
HNO $^3A''$	45.5	−2.0	−1.8	−0.4	−1.8	−2.0	−0.5
H_2	0.0	−0.5	−1.1	−1.1	−0.3	−0.9	−1.4
H_2NF	−5.0	−1.2	−0.9	−2.4	−1.2	−1.4	−0.7
H_2O	−57.8	0.1	0.1	−0.3	−0.1	−0.1	−0.2
HOOH	−32.5	0.5	0.8	0.1	0.1	−0.1	0.3
NH_2	45.1	−0.9	−1.0	−0.1	−0.8	−1.0	0.1
NH_3	−11.0	0.6	0.8	0.1	0.5	0.2	0.4
H_2NNH_2	22.8	1.3	1.7	0.8	1.0	0.6	1.1
ClO	24.3	2.3	2.4	2.1	0.8	1.0	1.0
FOF	5.9	0.7	1.3	−0.6	−0.1	−0.1	−0.7
ClNO	12.4	0.7	0.0	−0.8	1.2	0.4	0.9
NO $^2\Pi$	21.6	0.1	−0.1	−0.7	0.5	0.0	−0.5
N_2O	19.6	−0.4	0.3	0.6	0.2	0.6	1.0
O	59.6	−0.2	−0.2	−0.2	−0.1	−0.1	0.4
OClO	22.8	4.6	5.7	4.8	0.5	0.6	−0.5
$ClNO_2$	3.0	−0.7	0.1	−3.2	−0.2	−0.1	−0.6
NO_2	7.9	−0.4	0.4	−0.7	0.2	0.2	0.5
O_2 $^3\Sigma^-$	0.0	−0.1	0.4	2.4	−1.0	−1.1	1.6
$FONO_2$	2.4	−0.5	1.5	−2.3	−0.1	0.2	0.0
NO_3 $^2B_2$	17.6	0.0	2.3	1.5	0.8	1.8	3.9
$ONNO_2$	19.8	−0.3	0.5	−1.4	0.6	−0.1	1.2
O_3 $^1A_1$	34.1	0.2	1.3	−1.1	−0.8	−1.0	−1.6
O_2NNO_2	2.2	−1.3	1.0	−2.6	−0.3	−0.1	1.0
NF_2	8.5	−0.9	−1.2	−2.5	−0.8	−1.4	0.2
N	113.0	0.0	0.0	0.0	−0.3	−0.1	−1.5
FNNF cis	17.9	−0.5	−0.3	−3.3	−0.2	−0.3	−0.3
N_2	0.0	0.6	0.6	1.2	1.0	1.2	0.7
F	19.0	−0.1	−0.1	−0.1	−0.1	0.0	1.9
F_2	0.0	1.2	1.4	0.3	0.7	1.0	−0.2
Cl	29.0	0.0	0.0	0.0	−0.2	0.5	0.8
Cl_2	0.0	1.9	0.7	1.4	−0.4	−0.6	0.4
Si	107.6	−0.2	−0.2	−0.2	−0.2	1.1	−0.3
$SiCl_4$	−158.2	1.8	−0.5	1.4	−0.5	−0.4	−0.2
SiH_2 $^3B_1$	84.6	0.1	−1.6	1.1	0.1	−0.6	0.7
SiH_3	46.4	0.3	−0.7	0.2	0.0	−0.3	0.5
SiO	−24.6	0.2	−1.0	1.7	0.5	0.5	2.0
SiO_2	−66.6	−1.1	−3.0	0.0	−0.9	−1.7	−0.2
SiS	27.6	−0.9	−3.3	0.1	0.1	−0.1	0.0
PH_2	32.8	−0.5	−1.4	0.0	−0.5	−0.8	−0.5
P	75.6	0.0	0.0	0.0	0.3	0.7	−0.3

TABLE 3 (Continued)

	heat of formation (kcal/mol)						
		error = theory − experiment					
neutrals	experimental	raw-G3B3	raw-G3MP2B3	raw-G2	BAC-G3B3	BAC-G3MP2B3	BAC-G2
Reference Set							
PH $^3\Sigma^-$	56.8	−1.1	−2.1	0.8	−0.8	−1.3	0.4
P_2	34.2	0.6	−0.3	1.4	0.3	0.3	0.0
PN	42.8	−1.0	−0.8	0.0	0.0	0.3	0.3
H_2S	−4.9	0.3	−0.8	0.0	0.5	0.6	−0.4
S	66.2	−0.1	−0.1	−0.1	0.5	1.5	−0.3
SH	34.2	−0.5	−1.3	0.2	0.1	0.3	−0.2
SO $^3\Sigma^-$	1.2	0.3	0.5	2.7	−0.3	0.5	0.5
SO_2	−70.9	2.5	2.5	5.0	0.3	0.1	0.7
SO_3	−94.6	4.4	5.3	6.9	0.3	0.2	−0.6
SiF_4	−386.0	2.1	2.4	7.1	0.7	1.2	3.1
P_4	14.1	3.7	0.6	5.4	−0.1	−0.1	−1.9
PH_3	1.7	1.0	0.3	0.2	0.5	0.5	−0.1
$SiCl_2$	−40.3	0.8	−1.3	1.0	0.3	0.7	1.3
SF_6	−291.7	8.7	10.4	3.8	−0.2	−0.2	−17.4
ClSSCl	−4.0	1.6	−1.8	1.5	−0.7	−1.4	−1.9
$(CH_3)_2SO_2$	−89.2	3.0	4.2	3.8	−0.1	0.6	−0.3
$(CH_3)_3CSH$	−26.2	−1.0	−1.9	−1.4	−0.7	−0.4	−2.1
C_4H_8S	−8.2	0.5	−0.5	0.7	0.5	0.5	0.1
$-CHCHSC(CH_3)CH-$	20.0	−0.5	−2.8	1.5	−0.9	−2.1	0.2
$C_5H_{10}S$	−15.2	0.0	−1.0	0.1	−0.2	0.1	−0.8
$-CH_2SCH_2-$	19.6	−0.8	−1.8	−0.9	−0.3	−0.2	−0.8
Cl_2SO_2	−84.8	6.3	6.1	4.8	0.2	0.2	−1.3
$C_{10}H_8$	36.1	−1.2	−4.3		0.2	0.0	
Test Set							
C_2Cl_6	−32.1	−6.8	−8.8	−11.4	−7.3	−6.4	−7.7
C_2Cl_4	−3.0	−2.1	−4.7	−4.6	−2.2	−2.2	−1.8
C_2F_4	−157.9	−3.9	−4.1	−7.8	−3.4	−3.1	−1.3
$-CH_2CH_2NH-$	28.3	2.6	2.7	2.0	2.1	2.1	1.4
NCCN	73.8	−1.9	−1.5	0.9	−1.3	0.1	−0.3
$-CH{=}HCH_2-$	66.2	1.9	1.2	2.7	2.2	2.1	1.3
$-CH_2CHCHCH_2-$	34.7	4.4	3.5	5.3	4.6	4.5	3.6
$-CH_2C({=}CH_2)CH_2-$	47.9	−1.9	−2.6	−0.6	−1.6	−1.6	−2.3
$CH_3CH_2NO_2$	−24.4	−1.6	−0.2	−4.1	−1.1	−0.7	−2.4
CH_3CN	17.7	−0.6	−0.5	0.2	−0.4	0.2	2.2
CN	105.6	−0.7	−1.3	1.7	−0.5	−0.6	2.4
CO $^3\Pi$	114.3	−3.9	−4.8	−2.2	−3.7	−4.3	−2.0
FNO	−15.7	−5.5	−5.3	−7.7	−5.0	−5.3	−5.2
HNCO	−24.9	−4.3	−3.9	−4.7	−3.6	−3.0	−3.9
HNNH trans	50.9	−2.6	−2.8	−3.1	−2.4	−2.7	−3.5
HOF	−23.5	3.0	3.4	2.2	2.5	2.6	2.3
$HOSO_2$	−92.0	7.3	7.8	8.1	3.9	3.8	1.6
$O{=}C(NH_2)_2$	−58.7	3.0	4.3	1.8	3.1	3.9	2.8
O_3 CYClIC	70.0	−3.6	−3.3	−4.5	−4.2	−5.6	−4.3
$OHCH_2CH_2OH$	−93.9	2.5	3.0	1.2	2.7	3.0	2.3
SiH_3SiH_3	19.1	−1.7	−1.6	−3.0	−3.4	−3.3	−1.1
SiH_2 $^1A_1$	64.8	−1.8	−2.1	−2.5	−1.5	−0.8	−2.0
SiH_4	8.2	−1.1	−1.2	−2.3	−1.9	−1.9	−1.1
ClOO	23.3	5.2	5.7	6.4	4.2	4.5	5.2
C_2H_3	71.8	−1.6	−2.0	0.8	−1.4	−1.2	−0.7
CH_2S	24.3	3.1	2.0	3.4	4.1	4.1	4.0
CH $^2\Pi$	142.5	−1.5	−2.1	−0.6	−1.4	−1.5	−1.3
CH_2CHCCH	70.4	−1.8	−2.9	0.8	−1.1	−1.1	−0.6
HCCCCH	111.0	−1.6	−2.5	2.2	−0.8	−0.4	0.8
CH_3S ($^2A'$)	29.8	−0.9	−1.5	0.0	−0.3	−0.1	0.6
SCl_2	−4.2	3.2	0.9	0.6	1.0	0.5	−4.2
S_2	30.7	1.1	−0.6	3.3	1.2	1.3	0.9
C_2H_5Cl	−26.8	0.4	0.0	2.6	0.3	0.2	0.0
PF_3	−229.1	5.8	5.5	5.3	2.1	2.3	−4.4
PCl_3	−69.0	4.9	2.0	4.4	0.6	−0.2	0.2
PCl_5	−86.1	1.1	−2.2	0.4	−7.2	−7.8	−7.7
PF_5	−381.1	8.6	8.9	6.6	0.8	1.1	−14.1
PO	−9.0	−6.6	−10.6	3.0	−7.5	−11.3	0.2
PO_2 ($^2A_1$)	−69.6	1.8	1.1	2.3	−0.8	−1.5	−1.7
HOPO cis	−112.4	3.5	3.6	2.3	1.4	1.5	0.6
$HOPO_2$	−171.4	5.9	6.6	1.8	1.8	2.1	0.5
$(HO)_2P$	−90.1	3.0	3.0	3.5	1.3	1.4	0.7
$(HO)_2PO$	−158.8	4.6	4.8	7.1	1.1	1.0	0.9
$(HO)_3P$	−188.8	4.4	5.0	4.0	1.6	1.9	0.6

TABLE 3 (Continued)

	heat of formation (kcal/mol)						
		error = theory − experiment					
neutrals	experimental	raw-G3B3	raw-G3MP2B3	raw-G2	BAC-G3B3	BAC-G3MP2B3	BAC-G2
			Test Set				
$CClF_3$	−169.2	−0.5	−0.7	−5.7	−0.4	−0.3	−0.4
C_2F_6	−321.3	−1.9	−1.4	−9.4	−1.4	−1.1	−1.1
$POCl_3$	−136.0	7.0	5.7	6.9	−0.2	0.2	−1.8
CF_3CN	−118.4	−2.2	−1.9	−4.9	−1.6	−1.0	−1.3
ClF_3	−38.0	3.1	4.7	−0.4	−1.2	−0.2	−7.8
AlH_3	30.8	−0.3	0.3	−2.0	0.9	1.1	−1.8
AlF_3	−289.0	−0.4	−0.2	1.3	0.8	0.7	−7.9
$AlCl_3$	−139.7	−2.0	−2.6	−2.8	−1.3	−0.7	0.7
BH_3	21.0	2.2	3.9	1.3	2.2	3.7	−0.8
BF_3	−271.5	−1.0	−0.3	2.1	−1.2	−0.8	3.8
BCl_3	−96.7	−0.9	−1.2	−4.2	−1.6	−0.6	−19.7
AlH	59.6	−1.6	−1.7	−2.1	−0.6	−0.8	−1.2
AlF	−63.1	−2.5	−2.3	−1.8	−1.5	−1.4	−3.1
AlCl	−12.2	−2.1	−2.8	−1.7	−1.3	−1.5	−1.7
BH	106.6	−3.1	−3.2	−3.3	−2.9	−2.9	−4.0
BF	−27.7	0.5	0.1	−0.2	0.6	0.2	−10.2
BCl	41.2	0.4	−0.7	−1.1	0.3	−0.2	−6.4

[a] Note that the difference is taken to be theory minus experiment, the reverse of the difference defined in G3 references.[14,15,18,19]

TABLE 4: Overall Accuracy of Raw and BAC Corrected Quantum Chemistry Methods

	heat of formation at 298 K (kcal/mol)		
method	average error	RMS error	maximum error
	Reference Set[a]		
raw-G3B3	0.82	1.37	8.73
BAC-G3B3	0.44	0.56	1.76
raw-G3MP2B3	1.07	1.71	10.42
BAC-G3MP2B3	0.50	0.67	2.09
raw-G2	1.34	1.90	6.80
BAC-G2	0.69	0.90	2.68
	Test Set without Ions[b]		
raw-G3B3	1.38	2.16	8.73
BAC-G3B3	0.91	1.50	7.51
raw-G3MP2B3	1.61	2.47	10.56
BAC-G3MP2B3	0.96	1.66	11.31
	Test Set with Ions[c]		
raw-G3B3	1.32	2.04	8.73
BAC-G3B3	0.95	1.52	7.51
raw-G3MP2B3	1.60	2.38	10.56
BAC-G3MP2B3	1.04	1.71	11.31
	Set Containing Only Ions[d]		
raw-G3B3	1.09	1.55	5.41
BAC-G3B3	1.13	1.60	5.60
raw-G3MP2B3	1.57	2.00	5.20
BAC-G3MP2B3	1.40	1.85	5.70

[a] 155 molecules are used in the reference set. [b] 216 molecules are used in the test set with neutrals and without ions. [c] 273 molecules are used in the test set with ions. [d] 57 ions are used.

C. Assessment of the BAC-G3B3 and BAC-G3MP2B3 Procedures for Test Set of Molecules. In addition to the reference set, we have defined an extended test set of compounds used to test the predictive capabilities of BAC procedures. The test set includes additional neutrals, as well as ions and transition state structures from the first three rows of the periodic table, representing a diverse set of different chemical moieties. The test set includes molecules for which the accuracy of experimental values has not been as well validated and thus was not included in the reference set. Including such molecules in the reference set could have an adverse effect on defining the BAC parameters. In addition, the test set includes positive and negative ions for which the predictive capability of the BAC procedure has not yet been demonstrated.

To further discuss the accuracy of the BAC-G3B3, we have broken the discussion into several parts. First, we discuss the overall agreement between theory and experiment for the test set. Then, we discuss those compounds for which the BAC-G2 procedure has difficulties. Then, we discuss the set of compounds for which the G3 method has particular difficulty, involving interactions between second and third row elements, for which the G3X method was developed,[19] with particular attention to the PO_x species. We then discuss the special case of the boron and aluminum compounds, for which experimental data are sparse or lacking. Finally, we discuss the applicability of the BAC-G3B3 and BAC-G3MP2B3 procedures for cations and anions as well as for transition state structures.

First, we discuss the overall applicability of the BAC-G3B3 procedure for the test set. The average, RMS, and maximum errors in the heats of formation for the test set for the BAC-G3B3 and BAC-G3MP2B3 procedures, along with the raw G3B3 and G3MP2B3 methods, are listed in Table 4. We include an intermediate analysis for only the neutrals in the test set (excluding the anions and cations). As compared with the reference set, the errors for the larger test set are somewhat larger, as is to be expected. However, the errors are still quite small (average error of 0.91 and 0.96 vs 0.44 and 0.50 kcal/mol and the RMS error of 1.50 and 1.66 vs 0.56 and 0.67 kcal/mol). One cause for the error can be due to the complex electron correlation interactions between the electrons within the molecule, indicating that higher levels of electronic theory are still required. The other cause of error can be due to errors in the predicted experimental values.

Table S3 in the Supporting Information lists the compounds for which the BAC-G2 had deviations higher than 1 kcal/mol. The table includes compounds not only from the original reference set used for BAC-G2[24] but also from those in the extended test set. We observe that the BAC-G3B3 procedure has addressed many of the errors for those species for which BAC-G2 is not accurate within 2 kcal/mol. The NIST Computational Chemistry Comparison and Benchmark Database[29] has suggested alternative experimental heats of formation for some molecules whose heats of formation vary significantly from the experimental values used in this work. For example, Table S4 in the Supporting Information lists the compounds with sig-

TABLE 5: Errors in the BAC-G3B3 and G3X[19] Heats of Formation at 298 K for Selected Nonhydrogen Species in the G3/99 Test Set

	error in heat of formation (kcal/mol)			
compounds	G3X	raw-G3	BAC-G3B3	raw-G3B3
CO_2	−1.7	−1.7	−0.8	−1.6
SO_2	0.7	2.5	0.3	2.5
CF_4	−0.1	−0.2	0.3	0.0
CCl_4	−0.9	−0.2	−0.6	−0.2
COS	−3.2	−2.1	−0.6	−2.1
CS_2	−3.3	−3.0	−1.0	−3.0
$SiCl_4$	0.6	1.8	−0.5	1.8
N_2O	−0.7	−0.4	0.2	−0.4
ClNO	0.5	0.8	1.2	0.7
F_2O	1.0	0.7	−0.1	0.7
C_2F_4	−4.3	−3.9	−3.4	−3.9
SO_3	1.5	4.4	0.3	4.4
SiF_4	−2.3	1.1	0.7	2.1
PF_3	1.9	4.8	2.1	5.8
O_3	0.4	0.8	−0.8	0.2
ClF_3	0.4	1.9	−1.2	3.1
C_2Cl_4	−2.7	−3.4	−2.2	−2.1
CF_3CN	−2.2	−1.8	−1.6	−2.2
PF_5	1.8	7.1	0.8	8.6
SF_6	0.5	6.2	−0.2	8.7
P_4	2.2	4.2	−0.1	3.7
SCl_2	1.9	2.0	1.0	3.2
$POCl_3$	2.3	3.1	−0.2	7.0
PCl_5	−1.7	−2.4	−7.2	1.1
Cl_2O_2S	2.6	4.4	0.2	6.3
PCl_3	3.3	3.2	0.6	4.9
Cl_2S_2	−0.5	−0.1	−0.7	1.6
$SiCl_2$	0.1	−0.4	0.3	0.8
CF_3Cl	−0.1	−1.2	−0.4	−0.5
C_2F_6	−1.8	−2.8	−1.4	−1.9

TABLE 6: Heats of Formation of Phosphorus Oxides at 298 K Predicted by BAC-G3B3, G3X,[19] and G3X2[31] Methods[a]

	heat of formation (kcal/mol)				
species	G3X	G3X2	BAC-G3B3	BAC-G2	experimental sources
PO	−7.7	−9.0	−16.5 ± 4.0	−8.8	−6.7,[37] −5.6[36]
PO_2	−67.6	−69.6	−70.4 ± 2.9	−71.3	−67.3,[37] −75.1[38]
HOPO cis	−110.3	−112.3	−111.0 ± 2.3	−111.8	−110.6[39]
$HOPO_2$	−167.4	−170.5	−169.6 ± 4.2	−171.9	−168.8[39]
$(HO)_2P$	−88.3	−90.1	−88.8 ± 1.9	−89.4	
$(HO)_2PO$	−156.4	−158.8	−157.7 ± 3.6	−157.9	
$(HO)_3P$	−186.4	−188.8	−187.2 ± 3.0	−188.2	

[a] For $(HO)_2P$ and $(HO)_3P$, there is a lack of experimental data.

nificant changes in experimental heats of formation. Using the alternative heats of formation for those compounds would reduce the errors in the BAC-G3B3 predicted heats of formation. Those compounds would no longer be outliers (errors < 2 kcal/mol).

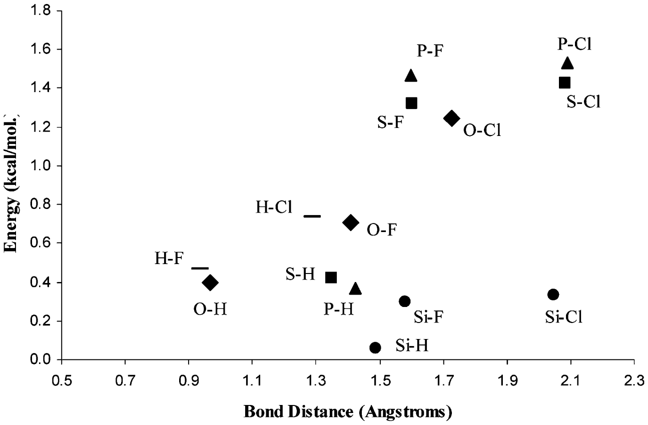

Figure 4. BAC factor $A_{ij}e^{-\alpha R_{ij}}$ for chemical bonds involving H, F, and Cl. BAC-G3B3 parameters are used for illustration purposes. For all of the cases, α is 3.0 Å^{-1}. Each point in the plot corresponds to a typical unsaturated single-bond bond distance. Because A_{ii} for C and N is 0, the correction factor for bonds between H, F and Cl, and C or O is 0.

The G3 method is known to have difficulties with elements of the third row, particularly when they involve hypervalent or dative bonding with elements of the second row, such as the sulfur−oxygen bond. The G3X method[19] was developed to remove some of the deficiencies in the G3 method, at the expense of increased computational time. In Table 5, we compare the results of the BAC-G3B3 procedure with the raw values for the G3 and G3X methods for the nonhydrogen species in the G3/99 test set suite.[14,19] Compounds containing C, N, O, F, Si, P, S, and Cl atoms are included in the table. Boron and aluminum compounds are discussed separately in Table 7.

We see that the BAC-G3B3 does very well overall. This includes both unsaturated carbon−sulfur bonds, for which the sulfur is electronegative, and sulfur−oxygen bonds, for which the sulfur is electropositive. The halogenated compounds tend to have uniformly lower heats of formation than the experimental values, consistent with a recent recommendation[30] that the experimental values of these compounds should be lowered.

While the G3X is an improvement over the G3 method, Mackie et al.[31] have extended the G3X method to include even larger basis sets and applied the new method, denoted G3X2, to phosphorus oxides. A single g polarization function for the third row G3Large basis set at the HF level yielded a G3XLarge basis set. The B3LYP/6-31G(2df,p) step has replaced the MP2(FU)/6-31G(d) method for geometry optimization and HF/6-31G(d) and MP2(FU)/6-31G(d) for the calculation of ZPEs. The G3X2 technique uses the G3XLarge basis set expansion correction at the MP2(full) level instead of the G3Large basis

TABLE 7: Comparison of BAC Heats of Formation at 298 K for Al and B Compounds[a]

	heat of formation (kcal/mol)				
species	BAC-G3B3	BAC-G3MP2B3	BAC-G2	experimental value	other sources
AlH_3	31.7	31.9	−1.8	30.8 ± 4.8	30.81[37]
AlF_3	−288.2	−288.3	−7.9	−289.0 ± 0.7	−289.0 ± 0.6[38]
$AlCl_3$	−141.0	−140.4	−7.7	−139.7 ± 1.2	−139.7 ± 0.7[38]
AlH	59.0	58.8	−1.2	59.6 ± 0.8	61.9 ± 4.8[38]
AlF	−64.5	−64.5	1.0	−63.1 ± 0.7	−63.5 ± 0.8[38]
AlCl	−13.7	−13.7	−1.7	−12.2 ± 0.7	−12.3 ± 1.5[38]
BH_3	23.2	24.7	24.1	21 ± 2.4	25.5 ± 2.4,[38] 23.80[41]
BF_3	−272.7	−272.3	−267.7	−271.5 ± 0.2[37]	−271.420,[36] −271.65[42]
BCl_3	−98.4	−97.3	−98.3	−96.68 ± 0.31	−96.3 ± 0.5,[38] −97.50,[41] −96.31[42]
BH	103.7	103.7	104.6	106.6 ± 1.7	105.8 ± 2.0,[38] 108.24,[41] 73.8[39]
BF	−27.1	−27.5		−27.7[33]	−27.7[42]
BCl	41.5	41.0	42.0	41.2 ± 6.0	33.8 ± 4,[38] 36.01,[41] 33.80[42]

[a] For AlH_3, there is a lack of experimental data; the value mentioned in the table is an estimate from theory.

TABLE 8: Comparison of Errors in Predicted Heats of Formation at 298 K for Ions

Anions

	heat of formation (kcal/mol)					
	experimental energies		predicted heat of formation			
ions	$\Delta H_f{}^0{}_{298}$ of neutral	electron affinity	BAC-G3B3	BAC-G3MP2B3	raw-G3B3	raw-G3MP2B3
P	75.6	17.2	1.0	2.5	0.5	1.7
S	66.2	47.9	0.6	1.3	−0.2	−0.5
CH	142.5	28.6	0.0	0.4	0.0	0.0
CH_2	93.4	15.0	1.0	0.6	0.8	0.2
CH_3	35.0	1.8	2.2	1.2	2.0	0.9
SiH_2	64.8	25.9	−0.6	−0.1	−0.7	−1.3
SiH_3	46.4	32.5	−0.1	0.1	0.0	−0.5
PH	56.8	23.8	0.6	0.9	0.1	−0.1
PH_2	32.8	29.3	−0.2	−0.6	−0.4	−1.4
SH	33.3	54.4	2.0	1.6	1.3	−0.3
C_2	200.2	75.5	−2.9	−3.8	−3.1	−4.6
CF_2	−43.5	4.1	−2.3	−2.1	−2.5	−2.7
SO_2	−70.9	25.5	0.6	1.1	2.1	2.6
C_2H	135.0	68.5	0.6	−0.8	0.1	−1.9
C_2H_3	71.8	15.4	−1.0	−2.4	−1.4	−3.3
C_3H_5	40.8	10.9	0.2	−1.1	−0.3	−2.2
CHO	10.3	7.2	0.0	−0.7	−0.6	−1.5
CHF	30.0	12.5	5.6	5.7	5.4	5.2
CH_3O	4.2	36.2	1.3	0.6	0.9	0.5
CH_3S	29.8	43.1	0.0	−0.6	−0.8	−2.2
CH_2S	24.3	10.7	4.5	4.3	3.6	2.3
C_2H_3O	80.6	42.1	1.3	0.8	0.8	0.1
OH	8.9	42.2	0.8	0.2	0.7	0.0
F	19.0	78.4	−0.3	−0.5	−0.4	−0.7
O	59.6	33.7	2.6	3.0	2.4	2.8
C	171.3	29.1	1.1	3.5	1.4	3.4
Cl	29.0	83.4	−0.1	−1.1	−0.2	−1.7
Cl_2	0.0	55.1	0.4	0.1	0.8	−0.7
O_2	0.0	10.1	1.1	1.8	1.5	2.6
CN	105.6	89.0	−0.7	−1.3	−1.1	−2.1
H_2N	45.1	17.8	1.3	−0.2	1.0	−0.3
HN	84.1	8.8	4.5	4.3	4.4	4.0

Cations

	heat of formation (kcal/mol)					
	experimental energies		predicted heat of formation			
ions	$\Delta H_f{}^0{}_{298}$ of neutral	ionization potential	BAC-G3B3	BAC-G3MP2B3	raw-G3B3	raw-G3MP2B3
Si	107.6	187.9	−0.5	−0.3	−0.6	−1.7
S	66.2	238.9	−1.4	−1.9	−1.9	−3.3
CH_4	−17.9	291.0	2.6	2.9	2.8	3.3
NH_3	−11.0	234.8	−0.4	−0.2	−0.1	0.5
SiH_4	8.2	253.7	−1.2	−3.1	0.2	−1.3
PH	56.8	234.1	0.3	−0.7	−0.2	−1.6
PH_2	32.8	226.5	−0.4	−0.7	−0.5	−1.5
SH	34.2	239.1	−1.1	−1.9	−1.5	−3.4
$SH_2(^2B_1)$	−4.9	241.4	−0.3	−0.6	−0.4	−1.8
$N_2\ ^2\Sigma$	0.0	359.3	1.0	1.1	0.7	0.7
O_2	0.0	278.3	−0.7	−0.9	0.4	1.1
S_2	30.7	215.8	0.8	0.9	1.0	−0.7
O	59.6	313.9	−1.4	−1.9	−1.3	−1.8
N	113.0	335.3	−0.8	−1.4	−0.7	−1.4
F	19.0	401.7	−0.7	−0.1	−0.5	0.0
C	171.3	259.7	−1.2	−1.9	−1.2	−2.2
CL	29.0	299.1	−1.8	−1.5	−1.5	−1.9
OH	8.9	300.2	−2.5	−3.2	−2.3	−3.1
H_2O	−57.8	291.0	−0.7	−0.6	−0.3	−0.3
H_2	0.0	355.7	−0.4	−0.1	−0.5	−0.2
HCCH	54.5	262.9	0.6	1.1	0.3	0.2
H_2CCH_2	12.5	242.4	0.5	1.3	0.3	0.8
CO	−26.4	323.1	0.1	−0.2	−0.3	−0.8
HCO	10.3	187.7	−0.4	−0.1	−1.0	−0.9
HCL	−22.1	294.0	−1.0	−0.6	−0.3	−0.8

set at the MP2(full) level. In Table 6, we have compared the enthalpies predicted by BAC-G3B3 against the values for G3X and G3X2 for the phosphorus oxide containing compounds. The results indicate a slight lowering of a couple of kcal/mol going from G3X to G3X2, consistent with the predicted values from the BAC-G3B3 and BAC-G2 procedures. This provides additional confirmation of the predictive capability of the BAC-G3B3 procedure for the phosphorus oxide containing species.

TABLE 9: Activation Energies (kcal/mol) Predicted by Different BAC Procedures[a]

reaction	BAC-G3B3	BAC-G3MP2B3	BAC-G2	BAC-hybrid	BAC-DFT	BAC-MP4
$H_2 + H \Leftrightarrow H + H_2$	8.0 (8.3)	7.6 (8.0)	9.2	8.7	7.6	8.8
	59.8	58.8	59.7	60.9	59.7	60.9
$CH_4 + OH \Leftrightarrow CH_3 + H_2O$	3.2 (3.6)	3.4 (4.0)	5.0	1.6	−0.5	3.2
	−6.6	−6.5	−3.8	−6.7	−9.8	−5.1
$H_2 + O \Leftrightarrow H + OH$	8.1 (8.5)	7.5 (8.6)	12.1	9.8	4.9	10.5
	67.2	66.6	70.6	69.4	66.0	70.3
$NH_3 + O \Leftrightarrow NH_2 + OH\ {}^3A'$	9.1 (9.5)	9.4 (9.8)	12.2	11.4	2.8	12.2
	58.1	58.0	61.5	59.8	53.8	61.1
$NH_3 + O \Leftrightarrow NH_2 + OH\ {}^3A''$	7.8 (8.2)	8.1 (8.5)	10.1	10.5	1.2	9.8
	56.8	56.7	59.4	58.9	52.2	58.7
$C_2H_4 + H \Leftrightarrow C_2H_5$	−0.9 (−0.6)	−1.3 (−0.7)	2.3	1.9	1.2	2.9
	63.7	63.1	66.2	67.7	66.1	67.3
$H + CO \Leftrightarrow HCO$	1.0 (1.0)	0.5 (0.7)	2.4	2.4	−4.6	2.4
	26.5	25.6	26.9	27.3	23.0	25.7
$C_2H_5 \Leftrightarrow C_2H_5$	39.8 (40.3)	39.1 (40.0)	40.6	39.9	38.7	42.3
	68.3	67.8	69.9	69.5	66.9	71.1
$HCN \Leftrightarrow HNC$	44.1 (45.3)	42.5 (44.5)	44.4	47.9	47.1	45.1
	75.1	73.8	75.1	78.3	78.9	76.9
$C_2H_5NO_2 \Leftrightarrow C_2H_4 + HONO$	45.9 (47.1)	44.8 (46.6)	48.3	46.4	41.3	48.5
	20.4	19.7	21.5	20.4	16.7	23.7
$C_2H_5Cl \Leftrightarrow C_2H_4 + HCl$	57.6 (58.1)	56.4 (57.5)	59.0	61.8	52.2	70.5
	31.1	29.8	32.1	34.9	24.0	43.3

[a] The first row for each column is the difference in the heats of formation of the transition state and the reactants. The corresponding raw G3B3 and G3MP2B3 values are given in parentheses. The second row represents the heats of formation of the transition state structure itself.

One of the dominant effects of the BAC procedure is to lower the energy relative to the raw G3B3 method for the bonding of P and S to the electronegative elements F, O, and Cl. This is achieved via the exponential term in the bondwise additive correction given in eq 5. Figure 4 shows the resulting BAC contribution for selected bond types. This lowering of the energy, for instance, brings the heats of formation for SO_2, SO_3, Cl_2SO_2, SF_6, PF_3, PF_5, $POCl_3$, and PCl_3 into significantly better agreement with experiment (see Table 5). The addition of the extended basis sets in the G3X and G3X2 methods also tends to lower the energy (see Tables 5 and 6).

The results for the PO and PCl_5 molecules stand out from the molecules in Tables 5 and 6. For PO, the BAC-G3B3 and BAC-G3MP2B3 methods are predicting too low an energy (see Table 6). The discrepancy for the PO molecule most likely is a pathological artifact of the G3 method itself, since the BAC corrections for PO only amount to 0.9 kcal/mol. The G3B3 and G3MP2B3 predicted values are significantly different from the G3X, G3X2, and G2 results, as well as from higher levels of theory involving extrapolated coupled cluster calculations, such as by Woon and Dunning,[32] Bauschlicher,[33] and Haworth and Backsay.[34] Occasionally, one or more of the individual steps in Gaussian-*n* methods can diverge. For instance, the G1 method for $C_2H_4^+$ differs by more than 100.0 kcal/mol from the G2 and G2MP2 values. For PO, the results for the G3 and G3B3 differ by 7.1 kcal/mol for a tiny change in bond distance, going from 1.472 to 1.499 Å. The electronic calculation for PO has a convergence problem in the electronic wave function, leading to a discrepancy in the resulting estimates of the MP2 energy in the QCISD(T) step. The unusually large difference of 4.0 kcal/mol between the G3B3 and the G3MP2B3 values (see Table 3) is indicative of a convergence problem in the G3 for the PO molecule.

The situation for the PCl_5 molecule is less clear. Our results suggest that the experimental value should be lower. Gurvich et al.[35] recommend a heat of formation of −90.0 rather than the −86.1 value taken from Chase et al.[36] The lower experimental value is consistent with the above observed trends from the other levels of theory. Whether or not the experimental heat of formation should be further lowered, as predicted by the BAC-G3B3 and BAC-G2 values, needs to be further investigated. In general, it is difficult to determine when the G3 methods themselves are having pathological difficulties as opposed to experimental data.

We now address the thermochemistry for molecules containing boron and aluminum. Few aluminum and boron compounds exist for use in the reference set of molecules, due to the limited experimental data with reasonable uncertainties. In the reference set of molecules, AlH_3, AlF_3, $AlCl_3$, AlH, AlF, and AlCl are used for aluminum compounds, while BH_3, BF_3, and BCl_3 are used for boron compounds. Because the two sets of compounds consist of limited types of atoms and bonds, they are not representative of various elements from the first three rows. The number of compounds is fewer than the total number of BAC parameters required for the BAC-G3B3 as well as BAC-G3MP2B3 methods. This introduces numerous choices of parameters or degrees of freedom that could address the errors for the few compounds. Hence, the B and Al compounds are used only to estimate the BAC parameters for B and Al, respectively. This prevents the BAC parameters for the other atoms and the overall results to be biased by the considerable uncertainties in experimental data for these small numbers of Al and B compounds. Table 7 compares the BAC predicted heats of formation of Al and B compounds. Unless otherwise indicated in the table, the current experimental values are taken from Gurvich et al.[35] We use the heat of formation of a BAC-G2 calculation for BH_3. The value recommended by Cox et al.[40] is used for BF_3.

Next, we report the results for anions and cations. The errors in the predicted heats of formation are reported in Table 8. We have defined the heats of formation to follow the ion convention rather than the electron convention[43−45] in which the heat capacity of the electron is ignored. Thus, the heat of formation of a positive ion is taken to be the heat of formation of the neutral molecule plus the ionization potential, while the heat of formation of a cation is taken to be the heat of formation of the neutral molecule minus the electron affinity. Overall, the results for the ions provide excellent agreement with experiment, as can be seen from the statistical error analysis in Table 4. The resulting errors in the heats of formation can be due either to the neutral molecule heat of formation or to measurements in the ionization potential or electron affinity. Because the geometries of the ions are very similar to those of the neutral molecules (excluding proton affinities), most of BAC corrections for a given ion−neutral pair tend to cancel. Thus, the BAC results are very similar to the excellent results provided by the raw G3B3 and G3MP2B3 methods themselves.

In Table 9, we compare the applicability of the BAC-G3B3 and BAC-G3MP2B3 procedures with previous BAC procedures[24] for determining activation energies for reactions. The activation energy represents the difference between the heats of formation of the transition state structure and reactants. Because errors can occur (or cancel) due to the accuracy of either the transition state structure or the reactants, we also provide the absolute heat of formation of the transition state structure.

Because the BAC corrections are small for the BAC-G3B3 and BAC-G3MP2B3 procedures and most of the BAC corrections cancel in the determination of the activation energy, the BAC-G3B3 and BAC-G3MP2B3 results are nearly identical to the raw G3B3 and G3MP2B3 results. For the most, the BAC-G3B3 and BAC-G3MP2B3 activation energies are very similar to each other but slightly lower than the BAC-G2 results. Part of the differences may be due to the use of the B3LYP method for optimizing the geometry and determining the frequencies. The same geometries and frequencies are used in the BAC-G3B3 and BAC-G3MP2B3 procedures as for the BAC-hybrid and BAC-DFT procedures.

IV. Summary and Conclusions

We have developed the BAC procedure for the G3B3 and G3MP2B3 quantum chemistry methods to improve the accuracy of predicted thermochemical properties of open and closed shell molecules containing elements from the first three rows of the periodic table. BAC-G3B3 and BAC-G3MP2B3 parameters have been developed for atomic, molecular, and bondwise corrections to heats of formation of molecules.

The usefulness of BAC procedure has been assessed by comparing the heats of formation predicted by the BAC-G3B3 and BAC-G3MP2B3 procedure against experimental values for a 273 molecule test set containing various chemical moieties, multireference configurations, isomers, and degrees of saturation. BAC corrections have significantly improved the overall accuracy as well as the accuracy for specific compounds. For the reference set, the average error for the BAC-G3B3 results is 0.44 kcal/mol as compared to 0.82 kcal/mol for the raw G3B3. For the extended test set with neutrals, the average error for the BAC-G3B3 results is 0.91 kcal/mol as compared to 1.38 kcal/mol for the raw G3B3.

As compared to former BAC-MP4 and BAC-G2 methods, BAC-G3B3 provides better estimates of thermochemistry for compounds involving the first three rows of the periodic table, consistent with the improved accuracy of the G3 methods themselves. Some of the molecules need to be reinvestigated experimentally and theoretically, since the reported experimental values in the literature may not be sufficiently accurate. In particular, better experimental data need to be determined for the B, Al, and P compounds in order to determine the true predictive capability of the BAC procedure for these compounds.

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Supporting Information Available: Table S1 showing the experimental heats of formation for molecules in the reference set, table S2 showing the heats of formation of molecules in the extended test set, table S3 showing the errors in BAC predicted heats of formation at 298 K for compounds with highest errors for BAC-G2 or BAC-G3B3, table S4 showing heats of formation at 298 K suggested by NIST Computational Chemistry Comparison and Benchmark Database,[29] and table S5 showing the differences in experimental heats of formation of molecules reported in various literature sources. This material is available free of charge via the Internet at http://pubs.acs.org.

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